

PATENT ABSTRACTS OF JAPAN

JS

(11)Publication number : 2003-147045

(43)Date of publication of application : 21.05.2003

(51)Int.Cl.

C08G 59/16

G02B 6/12

(21)Application number : 2001-350739

(71)Applicant : NIPPON KAYAKU CO LTD

(22)Date of filing : 15.11.2001

(72)Inventor : KOYANAGI TAKAO
YOKOSHIMA MINORU

(54) RESIN COMPOSITION FOR OPTICAL WAVE GUIDE, AND ITS CURED PRODUCT

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a resin composition for an optical wave guide, facilitating a step for forming an optical wave guide, and enabling multilayer wiring by light, and further to provide a cured product of the resin composition.

SOLUTION: This resin composition for the optical wave guide contains (A) a specific carboxy group-containing epoxy compound, (B) a compound containing the epoxy group except the component (A) and/or an oxetane compound, and (C) a cationic photoinitiator.

LEGAL STATUS

[Date of request for examination]

04.12.2003

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

3815605

[Date of registration]

16.06.2006

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.**** shows the word which can not be translated.

3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The resin constituent for optical waveguides characterized by containing the carboxyl group content epoxy compound (A) which is a reactant of the epoxy compound (a) which has at least two epoxy groups in a molecule, the compound (b) which has one carboxyl group and two hydroxyl groups in a molecule, and a polybasic acid anhydride (c), epoxy group content compounds other than the (A) component and/or an oxetane compound (B), and an optical cationic initiator (C) [claim 2] The hardened material of the resin constituent for optical waveguides according to claim 1

[Translation done.]

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.**** shows the word which can not be translated.

3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This inventions are general optics and the microoptics field, and relate to the resin constituent for optical waveguides which can be used for various optical integrateds circuit or optical patchboards etc. which are further used in the field of optical communication or optical information processing, and its hardened material.

[0002]

[Description of the Prior Art] As for the optical waveguide used in optical information processing and the optical-communication field, examination prospers in recent years aiming at integration, micrifying, advanced features, and low-pricing. Quartz system optical waveguide has actually come to be put in practical use at a part of optical-communication field. Moreover, examination of the macromolecule waveguide which can choose the simple producing method using a cheap ingredient is also prosperous. For example, the approach using the application, the photosensitive giant molecule, or resist of an approach used for semi-conductor processings, such as lithography and etching, can be mentioned. Although irradiate ultraviolet rays through a pattern film, the approach of removing and forming an unexposed part with solvents etc. is performed in the approach of forming a core especially using a photosensitive macromolecule and forming waveguide, the production approach is simple and it is suitable for low-pricing. It is necessary to use a solvent for patternizing, and there is a problem of insurance and an environment. Moreover, a problem is in the homogeneity of the core configuration which the transparency of a photosensitive macromolecule is inadequate, and absorption loss is high or is produced, and repeatability, scattering loss may become high and the optical waveguide in which the waveguide property has the engine performance comparable as quartz system optical waveguide is not produced.

[0003]

[Problem(s) to be Solved by the Invention] The technical problem mentioned above is solved, and the object of this invention can be patternized in a dilute-alkali water solution, and is to offer the resin constituent for optical waveguides with which are simultaneously satisfied of the low price which is excellent in workability, and high performance-ization, and its hardened material.

[0004]

[Means for Solving the Problem] The resin constituent for optical waveguides with which this invention person etc. uses a specific carboxyl group content epoxy compound (A) and epoxy group content compounds other than the (A) component (B) as a principal component as a result of wholeheartedly examination. It can patternize [that a refractive index can be controlled somewhat freely by changing a presentation] by removing an unexposed part with a dilute-alkali water solution. It came to complete a header and this invention for excelling in light transmission nature, when it applies to the core section and the cladding layer of optical waveguide, and excelling in surface smoothness extremely.

[0005] Namely, this invention (1) In a molecule, at least two epoxy groups. The carboxyl group content epoxy compound (A) which is a reactant of the epoxy compound (a) which it has, the

compound (b) which has one carboxyl group and two hydroxyl groups in a molecule, and a polybasic acid anhydride (c), and epoxy group content compounds other than the (A) component And/or, it is related with the hardened material of the resin constituent for optical waveguides characterized by containing an oxetane compound (B) and an optical cationic initiator (C), and the resin constituent for optical waveguides given in (2) and (1).

[0006]

[The gestalt of operation of this invention] The resin constituents for optical waveguides of this invention are the carboxyl group content epoxy compound (A) which is a reactant of the epoxy compound (a) which has at least two epoxy groups in a molecule, the compound (b) which has one carboxyl group and two hydroxyl groups in a molecule, and a polybasic acid anhydride (c), epoxy group content compounds other than the (A) component and/or an oxetane compound (B), and mixture with an optical cationic initiator (C).

[0007] In this invention, a carboxyl group content epoxy compound (A) is used. A carboxyl group content epoxy compound (A) can be obtained by making the epoxy compound (a) which has at least two epoxy groups in a molecule, and the compound (b) which has one carboxyl group and two hydroxyl groups in a molecule react, and subsequently making a polybasic acid anhydride (c) react.

[0008] Here as an example of an epoxy compound (a) of having at least two epoxy groups in a molecule 3, 4-epoxycyclohexyl methyl -3, 4-epoxy cyclohexane carboxylate, 3, 4-epoxycyclohexyl ethyl -8, 4-epoxy cyclohexane carboxylate, 2-(3, 4-epoxycyclohexyl -5, 5-spiro -3, 4-epoxy) cyclohexane-m-dioxane, A bis(3, 4-epoxycyclohexyl) horse mackerel peat, a bis(3, 4-epoxycyclohexyl methyl) horse mackerel peat, As the bis(3, 4-epoxycyclohexyl) ether, a bis(3, 4-epoxycyclohexyl) diethyl siloxane, and a commercial item The Daicel Chemical Industries, Ltd. make, such as the SEROKI side 2021 (weight per epoxy equivalent 128-145) and the SEROKI side 2080 (weight per epoxy equivalent 190-210), 2 functionality alicyclic epoxy compound, EPOLEAD GT-301 (weight per epoxy equivalent 200-220), The Daicel Chemical Industries, Ltd. make, such as EPOLEAD GT-401 (weight per epoxy equivalent 210-235), 3 and 4 functionality alicyclic epoxy compound, EHPE (weight per epoxy equivalent 170-190, 70-90 degrees C of softening temperatures), Alicyclic epoxy compounds, such as the Daicel Chemical Industries, Ltd. make, such as EHPEL3150CE, and a solid alicyclic epoxy compound (a-1), The bisphenol A mold epoxy resin, a bisphenol female mold epoxy resin, Hydrogenation bisphenol A diglycidyl ether, bisphenol hexafluoroacetone diglycidyl ether, Tetra-bromine bisphenol A diglycidyl ether, 1, 3-bis (1-(2, 3-epoxy propoxy)-1-trifluoromethyl - 2, 2, and 2-trifluoroethyl) benzene, 1, 4-bis(1-(2, 3-epoxy propoxy)-1-trifluoromethyl - 2, 2, and 2-trifluoroethyl) cyclohexyl, A 4 and 4'-bis(2, 3-epoxy propoxy) octafluoro biphenyl, Glycidyl ether compounds (a-2), such as a phenol novolak mold epoxy resin, a cresol novolak mold epoxy resin, and a tris phenol methane mold epoxy resin, etc. can be mentioned.

[0009] Moreover, as an example of a compound (b) of having one carboxyl group and two hydroxyl groups, dimethylol propionic acid, a dimethylol acetic acid, dimethylol butanoic acid, a dimethylol valeric acid, a dimethylol caproic acid, etc. can be mentioned into a molecule.

[0010] Furthermore, as an example of a polybasic acid anhydride (c), a maleic anhydride, a succinic anhydride, phthalic anhydride, tetrahydro phthalic anhydride, hexahydro phthalic anhydride, methyl hexahydro phthalic anhydride, trimellitic acid, etc. can be mentioned.

[0011] Making 0.05-0.7Eq of carboxyl groups in the above and a compound (b) react makes 0.1-0.5Eq react preferably desirable especially to 1Eq of epoxy groups in the above and an epoxy compound (a). (a) It is desirable to make 0.1-1.0Eq of anhydride radicals in a polybasic acid anhydride (c) react to 1Eq of hydroxyl groups in the reactant of a component and the (b) component.

[0012] It is desirable to use a catalyst, in order to promote a reaction, when making the above, the (a) component, and the (b) component react. As an example of the catalyst which can be used, they are benzyl dimethylamine, methyl triethyl ammoniumchloride, a triphenyl stibine, triphenyl phosphine, etc. As a desirable catalyst, triphenyl phosphine can be mentioned especially. (a) It is desirable by oxidizing with a peroxide etc. and making triphenyl phosphine after reaction termination of a component and the (b) component, and in reaction mixture into

triphenyl phosphine oxide to inactivate the catalytic activity of triphenyl phosphine.

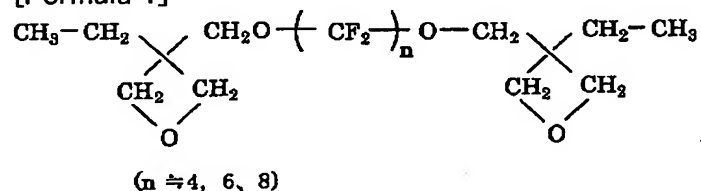
[0013] A diluent can also be used in a reaction. Solvents can be mentioned as an example of the diluent which can be used. As an example of solvents, ester, such as lactone, such as ether, such as aromatic hydrocarbon, such as ketones, such as ethyl methyl ketone and a cyclohexanone, toluene, and a xylene, and a tetrahydrofuran, gamma-butyrolactone, and epsilon-caprolactone, ethyl acetate, butyl acetate, carbitol acetate, and butyl-cellosolve acetate, can be mentioned. 70-110 degrees C is desirable especially desirable, and reaction temperature is 90-100 degrees C. 15 - 35 hours of reaction time are desirable.

[0014] (a) The reaction temperature of the hydroxyl group in the reactant of a component and the (b) component and the anhydride radical in the (c) component has desirable 70-110 degrees C, and 5 - 20 hours of reaction time are desirable.

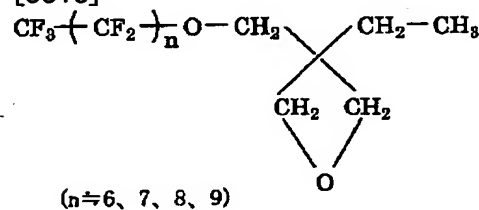
[0015] 10-100 are desirable especially desirable, and the acid numbers (mgKOH/g) of the carboxyl group content epoxy compound (A) which is an obtained product are 30-80. 200-700 are desirable especially desirable, and weight per epoxy equivalent is 250-500.

[0016] In this invention, the epoxy group content compounds and/or oxetane compounds (B) other than the (A) component are used. (B) As an example of a component, it is epoxy group content compound [, such as the above, an alicyclic epoxy compound (a-1), and a glycidyl ether compound (a-2),] (B-1), 3-ethyl-3-hydroxymethyloxetane, 1, and 4-bis[(3-ethyl-3-OKISETA nil methoxy) methyl] benzene and [0017].

[Formula 1]



[0018]



[0019] Oxetane compounds (B-2), such as a silicon denaturation oxetane compound, etc. can be mentioned.

[0020] An optical cationic initiator (C) is used in this invention. As an example of the optical cationic initiator (C) which can be used, if it reacts with an epoxy group by ultraviolet rays, although it is good, aromatic series iodonium salt, such as aromatic series sulfonium salt, such as aromatic series diazonium salt, such as P-methoxybenzene diazonium hexafluorophosphate, and triphenylsulfonium hexafluorophosphate, and diphenyliodonium hexafluorophosphate, aromatic series iodosyl salt, an aromatic series sulfoxonium salt, a metallocene compound, etc. will be mentioned anything, for example.

[0021] As an operating rate of the above and (A) - (C) component, among the resin constituent for optical waveguides of this invention (A) To the component 100 weight section, the 5 - 200 weight section is desirable especially desirable, and the (B) component is the 10 - 100 weight section, and receives the total amount 100 weight section of (A)+ (B) component. (C) 0.01 - 10 weight section is desirable especially desirable, and a component is 0.1 - 5 weight section.

[0022] In addition, in this invention, when required, optical cationic polymerization accelerators (an example, 9, a 10-dimethoxy-2-ethyl-anthracene, 9, 10-diethoxy anthracene, 2-ethyl thioxan ton, etc.), a silane coupling agent, a titanium system coupling agent, a flexible grant agent, a property modifier, etc. can be added. The property of a resin constituent can be reformed for these ingredients independent or by mixing and adding to a principal component.

[0023] for example, as an example of the silane coupling agent added in order to raise the adhesive property of the resin constituent of this invention gamma-aminopropyl trimethoxysilane, gamma-aminopropyl triethoxysilane, N-beta-(aminoethyl)-gamma-aminopropyl trimethoxysilane, N-beta-(aminoethyl)-gamma-aminopropyl triethoxysilane, N-beta-(aminoethyl)-beta-(aminoethyl)-gamma-aminopropyl methyl dimethoxysilane, gamma-mercaptopropyltrimethoxysilane, gamma-mercaptopropyl triethoxysilane, Gamma-methacryloxypropyl trimethoxy silane, gamma-glycidoxypropyltrimethoxysilane, A N-beta-(N-vinylbenzyl aminoethyl)-gamma-aminopropyl trimethoxysilane hydrochloride, Methyl trimethoxysilane, methyl triethoxysilane, vinyltriacetoxysilane, Gamma-chloropropyltrimethoxysilane, hexamethyldisilazane, gamma-ANIRINO propyltrimethoxysilane, vinyltrimethoxysilane, Octadecyl dimethyl [3-(trimethoxysilyl) propyl] ammoniumchloride, gamma-chloropropyl methyl dimethoxysilane, gamma-mercaptopropylmethyl dimethoxysilane, Methyltrichlorosilane, vinyltriethoxysilane, gamma-methacryloxypropyl tris (2-methoxyethoxy) silane, beta-(3, 4-epoxycyclohexyl) ethyltrimethoxysilane, etc. are mentioned.

[0024] The resin constituent of this invention can mix (A) - (C) component, the aforementioned coupling agent, etc., and can be dissolved, and the specified substance can be obtained by filtrating in a clean room etc. as occasion demands.

[0025] As the production approach of the optical waveguide in this invention, a clad is [0026] as the example, although it differs a little in the case where the same ultraviolet-rays hardening resin as the case where usual macromolecule resin is used, and core material is used. (1) Apply resin with a refractive index smaller than the core used as a lower layer clad to the substrate of arbitration. Stoving etc. removes a solvent after spreading. When using ultraviolet-rays hardening resin here, it hardens by irradiating ultraviolet rays.

(2) Through the negative mask which applies the resin constituent of this invention used as a core on this, next has a waveguide pattern, irradiate ultraviolet rays and harden them. Then, this sample is developed with a dilute-alkali water solution, for example, 3% diethanolamine water solution, only the optical exposure section is hardened according to a mask pattern, and a waveguide pattern can be produced.

(3) After that, apply the macromolecule resin or ultraviolet-rays hardening resin for clads on this, and harden by solvent clearance or ultraviolet rays. It is more suitable it to be desirable that it is the same refractive index as for the clad of the core lateral portion formed in a lower layer clad and a list at the end here and the upper part, and to be the same ingredient. When ultraviolet-rays hardening resin is used for a clad, flattening of the maximum top-face front face can be carried out. In this case, what is necessary is to attain multilayer optical wiring, and just to repeat (2) and (3), when multilayering.

[0027]

[Example] Hereafter, although an example explains this invention still more concretely, this invention is not limited to these examples.

Hydrogenation bisphenol A diglycidyl ether 353g, (Synthetic example 1 of a carboxyl group content epoxy compound (A)) 80.4g [of dimethylol propionic acid] and triphenyl phosphine 0.8g is taught. A reaction will be ended, if it reacts at 95 degrees C for about 10 hours and the acid number (mgKOH/g) of reaction mixture becomes 0.5 or less. Subsequently, tert-butyl peroxide 2-ethylhexyl carbonate 0.8g is taught at 80 degrees C. It reacted for about 3 hours, and triphenyl phosphine in reaction mixture was oxidized to triphenyl phosphine oxide, subsequently 60g of succinic anhydrides was taught at 90 degrees C, it reacted for about 5 hours, and the product (A-1) of weight per epoxy equivalent 353 and the acid number (mgKOH/g) 68.3 was obtained.

[0028] The resin constituent (a) prepared from product [which were obtained in the example 1 of example 1 composition] (A-1)g [70] and 3, 4-epoxycyclohexyl methyl -3, and 4-epoxy cyclohexane carboxylate 20g, bisphenol A diglycidyl ether 10g, and screw [4-(diphenyl sulfonium) phenyl] sulfide-screw hexafluorophosphate 3g was prepared. The refractive index after hardening of this resin constituent (a) was 1.519 on the wavelength of 589nm.

[0029] 60g (A-1) of next, products obtained in the synthetic example 1 on the silicon substrate, EPOLEAD GT-301(Daicel Chemical Industries, Ltd. make, weight-per-epoxy-equivalent 210, 3 functionality alicyclic epoxy compound) 5g, 1, 3-screw (1-(2, 3-epoxy propoxy)-1-trifluoromethyl

- 2, 2, and 2-trifluoroethyl) The resin constituent (b) prepared from benzene 35g and screw [4-(diphenyl sulfonium) phenyl] sulfide-screw hexafluorophosphate 3g It applied with the spin coat, ultraviolet rays were irradiated two times 2500 mJ/cm all over the, and the 10-micrometer lower cladding layer was produced.

[0030] Next, the above and a resin constituent (a) were applied to the thickness of 5 micrometers with the spin coat on this lower cladding layer. In addition, the refractive index after hardening of a lower cladding layer was 1.491 on the wavelength of 589nm.

[0031] Next, ultraviolet rays were irradiated through the negative mask which has a waveguide pattern, this sample was developed in the diethanolamine water solution 3% after that, and the waveguide pattern was produced. Then, on this waveguide pattern and a lower cladding layer, the above and a resin constituent (b) were applied to the thickness of 15 micrometers, ultraviolet rays are irradiated, and were stiffened, and optical waveguide was produced. The multimode channel waveguide which has the core which consists of a hardened material of the resin constituent (a) of the lower cladding layer, up cladding layer, and refractive index 1.530 which consist of a hardened material of the resin constituent (b) of the refractive index 1.515 after hardening by this actuation was producible. It was 0.30 dB/cm, as a result of starting the obtained optical waveguide in die length of 5cm and investigating photoconductive wave loss using helium-Ne laser light with a wavelength of 633nm.

[0032]

[Effect of the Invention] Production of the optical waveguide concerning this invention is simple, and is a resin constituent with which quality macromolecule optical waveguide is obtained. Therefore, the resin constituent for optical waveguides of this invention has the advantageous application to the optical waveguide die parts which mass production needs.

[Translation done.]

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

TECHNICAL FIELD

[Field of the Invention] This inventions are general optics and the microoptics field, and relate to the resin constituent for optical waveguides which can be used for various optical integrateds circuit or optical patchboards etc. which are further used in the field of optical communication or optical information processing, and its hardened material.

[Translation done.]

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

PRIOR ART

[Description of the Prior Art] As for the optical waveguide used in optical information processing and the optical-communication field, examination prospers in recent years aiming at integration, micrifying, advanced features, and low-pricing. Quartz system optical waveguide has actually come to be put in practical use at a part of optical-communication field. Moreover, examination of the macromolecule waveguide which can choose the simple producing method using a cheap ingredient is also prosperous. For example, the approach using the application, the photosensitive giant molecule, or resist of an approach used for semi-conductor processings, such as lithography and etching, can be mentioned. Although irradiate ultraviolet rays through a pattern film, the approach of removing and forming an unexposed part with solvents etc. is performed in the approach of forming a core especially using a photosensitive macromolecule and forming waveguide, the production approach is simple and it is suitable for low-pricing It is necessary to use a solvent for patternizing, and there is a problem of insurance and an environment. Moreover, a problem is in the homogeneity of the core configuration which the transparency of a photosensitive macromolecule is inadequate, and absorption loss is high or is produced, and repeatability, scattering loss may become high and the optical waveguide in which the waveguide property has the engine performance comparable as quartz system optical waveguide is not produced.

[Translation done.]

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.**** shows the word which can not be translated.

3.In the drawings, any words are not translated.

EFFECT OF THE INVENTION

[Effect of the Invention] Production of the optical waveguide concerning this invention is simple, and is a resin constituent with which quality macromolecule optical waveguide is obtained. Therefore, the resin constituent for optical waveguides of this invention has the advantageous application to the optical waveguide die parts which mass production needs.

[Translation done.]

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.**** shows the word which can not be translated.

3.In the drawings, any words are not translated.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] The technical problem mentioned above is solved, and the object of this invention can be patternized in a dilute-alkali water solution, and is to offer the resin constituent for optical waveguides with which are simultaneously satisfied of the low price which is excellent in workability, and high performance-ization, and its hardened material.

[Translation done.]

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.***** shows the word which can not be translated.

3.In the drawings, any words are not translated.

MEANS

[Means for Solving the Problem] The resin constituent for optical waveguides with which this invention person etc. uses a specific carboxyl group content epoxy compound (A) and epoxy group content compounds other than the (A) component (B) as a principal component as a result of wholeheartedly examination It can patternize [that a refractive index can be controlled somewhat freely by changing a presentation] by removing an unexposed part with a dilute-alkali water solution, It came to complete a header and this invention for excelling in light transmission nature, when it applies to the core section and the cladding layer of optical waveguide, and excelling in surface smoothness extremely.

[0005] Namely, this invention (1) In a molecule, at least two epoxy groups The carboxyl group content epoxy compound (A) which is a reactant of the epoxy compound (a) which it has, the compound (b) which has one carboxyl group and two hydroxyl groups in a molecule, and a polybasic acid anhydride (c), and epoxy group content compounds other than the (A) component And/or, it is related with the hardened material of the resin constituent for optical waveguides characterized by containing an oxetane compound (B) and an optical cationic initiator (C), and the resin constituent for optical waveguides given in (2) and (1).

[0006]

[The gestalt of operation of this invention] The resin constituents for optical waveguides of this invention are the carboxyl group content epoxy compound (A) which is a reactant of the epoxy compound (a) which has at least two epoxy groups in a molecule, the compound (b) which has one carboxyl group and two hydroxyl groups in a molecule, and a polybasic acid anhydride (c), epoxy group content compounds other than the (A) component and/or an oxetane compound (B), and mixture with an optical cationic initiator (C).

[0007] In this invention, a carboxyl group content epoxy compound (A) is used. A carboxyl group content epoxy compound (A) can be obtained by making the epoxy compound (a) which has at least two epoxy groups in a molecule, and the compound (b) which has one carboxyl group and two hydroxyl groups in a molecule react, and subsequently making a polybasic acid anhydride (c) react.

[0008] Here as an example of an epoxy compound (a) of having at least two epoxy groups in a molecule 3, 4-epoxycyclohexyl methyl -3, 4-epoxy cyclohexane carboxylate, 3, 4-epoxycyclohexyl ethyl -8, 4-epoxy cyclohexane carboxylate, 2-(3, 4-epoxycyclohexyl -5, 5-spiro -3, 4-epoxy) cyclohexane-m-dioxane, A bis(3, 4-epoxycyclohexyl) horse mackerel peat, a bis(3, 4-epoxycyclohexyl methyl) horse mackerel peat, As the bis(3, 4-epoxycyclohexyl) ether, a bis(3, 4-epoxycyclohexyl) diethyl siloxane, and a commercial item The Daicel Chemical Industries, Ltd. make, such as the SEROKI side 2021 (weight per epoxy equivalent 128-145) and the SEROKI side 2080 (weight per epoxy equivalent 190-210), 2 functionality alicyclic epoxy compound, EPOLEAD GT-301 (weight per epoxy equivalent 200-220), The Daicel Chemical Industries, Ltd. make, such as EPOLEAD GT-401 (weight per epoxy equivalent 210-235), 3 and 4 functionality alicyclic epoxy compound, EHPE (weight per epoxy equivalent 170-190, 70-90 degrees C of softening temperatures), Alicyclic epoxy compounds, such as the Daicel Chemical Industries, Ltd. make, such as EHPEL3150CE, and a solid alicyclic epoxy compound (a-1), The bisphenol A mold epoxy resin, a bisphenol female mold epoxy resin, Hydrogenation bisphenol A diglycidyl ether,

bisphenol hexafluoroacetone diglycidyl ether, Tetra-bromine bisphenol A diglycidyl ether, 1, 3-bis(1-(2, 3-epoxy propoxy)-1-trifluoromethyl - 2, 2, and 2-trifluoroethyl) benzene, 1, 4-bis(1-(2, 3-epoxy propoxy)-1-trifluoromethyl - 2, 2, and 2-trifluoroethyl) cyclohexyl, A 4 and 4'-bis(2, 3-epoxy propoxy) octafluoro biphenyl, Glycidyl ether compounds (a-2), such as a phenol novolak mold epoxy resin, a cresol novolak mold epoxy resin, and a tris phenol methane mold epoxy resin, etc. can be mentioned.

[0009] Moreover, as an example of a compound (b) of having one carboxyl group and two hydroxyl groups, dimethylol propionic acid, a dimethylol acetic acid, dimethylol butanoic acid, a dimethylol valeric acid, a dimethylol caproic acid, etc. can be mentioned into a molecule.

[0010] Furthermore, as an example of a polybasic acid anhydride (c), a maleic anhydride, a succinic anhydride, phthalic anhydride, tetrahydro phthalic anhydride, hexahydro phthalic anhydride, methyl hexahydro phthalic anhydride, trimellitic acid, etc. can be mentioned.

[0011] Making 0.05-0.7Eq of carboxyl groups in the above and a compound (b) react makes 0.1-0.5Eq react preferably desirable especially to 1Eq of epoxy groups in the above and an epoxy compound (a). (a) It is desirable to make 0.1-1.0Eq of anhydride radicals in a polybasic acid anhydride (c) react to 1Eq of hydroxyl groups in the reactant of a component and the (b) component.

[0012] It is desirable to use a catalyst, in order to promote a reaction, when making the above, the (a) component, and the (b) component react. As an example of the catalyst which can be used, they are benzyl dimethylamine, methyl triethyl ammoniumchloride, a triphenyl stibine, triphenyl phosphine, etc. As a desirable catalyst, triphenyl phosphine can be mentioned especially. (a) It is desirable by oxidizing with a peroxide etc. and making triphenyl phosphine after reaction termination of a component and the (b) component, and in reaction mixture into triphenyl phosphine oxide to inactivate the catalytic activity of triphenyl phosphine.

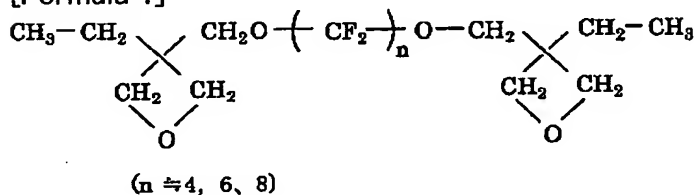
[0013] A diluent can also be used in a reaction. Solvents can be mentioned as an example of the diluent which can be used. As an example of solvents, ester, such as lactone, such as ether, such as aromatic hydrocarbon, such as ketones, such as ethyl methyl ketone and a cyclohexanone, toluene, and a xylene, and a tetrahydrofuran, gamma-butyrolactone, and epsilon-caprolactone, ethyl acetate, butyl acetate, carbitol acetate, and butyl-cellosolve acetate, can be mentioned. 70-110 degrees C is desirable especially desirable, and reaction temperature is 90-100 degrees C. 15 - 35 hours of reaction time are desirable.

[0014] (a) The reaction temperature of the hydroxyl group in the reactant of a component and the (b) component and the anhydride radical in the (c) component has desirable 70-110 degrees C, and 5 - 20 hours of reaction time are desirable.

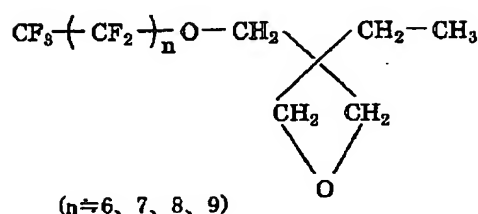
[0015] 10-100 are desirable especially desirable, and the acid numbers (mgKOH/g) of the carboxyl group content epoxy compound (A) which is an obtained product are 30-80. 200-700 are desirable especially desirable, and weight per epoxy equivalent is 250-500.

[0016] In this invention, the epoxy group content compounds and/or oxetane compounds (B) other than the (A) component are used. (B) As an example of a component, it is epoxy group content compound [, such as the above, an alicyclic epoxy compound (a-1), and a glycidyl ether compound (a-2),] (B-1), 3-ethyl-3-hydroxymethyloxetane, 1, and 4-bis[(3-ethyl-3-OKISETA nil methoxy) methyl] benzene and [0017].

[Formula 1]



[0018]



[0019] Oxetane compounds (B-2), such as a silicon denaturation oxetane compound, etc. can be mentioned.

[0020] An optical cationic initiator (C) is used in this invention. As an example of the optical cationic initiator (C) which can be used, if it reacts with an epoxy group by ultraviolet rays, although it is good, aromatic series iodonium salt, such as aromatic series sulfonium salt, such as aromatic series diazonium salt, such as P-methoxybenzene diazonium hexafluorophosphate, and triphenylsulfonium hexafluorophosphate, and diphenyliodonium hexafluorophosphate, aromatic series iodosyl salt, an aromatic series sulfoxonium salt, a metallocene compound, etc. will be mentioned anything, for example.

[0021] As an operating rate of the above and (A) - (C) component, among the resin constituent for optical waveguides of this invention (A) To the component 100 weight section, the 5 - 200 weight section is desirable especially desirable, and the (B) component is the 10 - 100 weight section, and receives the total amount 100 weight section of (A)+ (B) component. (C) 0.01 - 10 weight section is desirable especially desirable, and a component is 0.1 - 5 weight section.

[0022] In addition, in this invention, when required, optical cationic polymerization accelerators (an example, 9, a 10-dimethoxy-2-ethyl-anthracene, 9, 10-diethoxy anthracene, 2-ethyl thioxan ton, etc.), a silane coupling agent, a titanium system coupling agent, a flexible grant agent, a property modifier, etc. can be added. The property of a resin constituent can be reformed for these ingredients independent or by mixing and adding to a principal component.

[0023] for example, as an example of the silane coupling agent added in order to raise the adhesive property of the resin constituent of this invention gamma-aminopropyl trimethoxysilane, gamma-aminopropyl triethoxysilane, N-beta-(aminoethyl)-gamma-aminopropyl trimethoxysilane, N-beta-(aminoethyl)-gamma-aminopropyl triethoxysilane, N-beta-(aminoethyl)-beta-(aminoethyl)-gamma-aminopropyl methyl dimethoxysilane, gamma-mercapto propyltrimethoxysilane, gamma-mercapto propyl triethoxysilane, Gamma-methacryloxypropyl trimethoxy silane, gamma-glycidoxypropyltrimetoxysilane, A N-beta-(N-vinylbenzyl aminoethyl)-gamma-aminopropyl trimethoxysilane hydrochloride, Methyl trimetoxysilane, methyl triethoxysilane, vinyltriacetoxysilane, Gamma-chloropropyltrimetoxysilane, hexamethyldisilazane, gamma-ANIRINO propyltrimethoxysilane, vinyltrimetoxysilane, Octadecyl dimethyl [3-(trimethoxysilyl) propyl] ammoniumchloride, gamma-chloropropyl methyl dimethoxysilane, gamma-mercaptpropylmethyl dimethoxysilane, Methyltrichlorosilane, vinyltriethoxysilane, gamma-methacryloxypropyl tris (2-methoxyethoxy) silane, beta-(3, 4-epoxycyclohexyl) ethyltrimethoxysilane, etc. are mentioned.

[0024] The resin constituent of this invention can mix (A) - (C) component, the aforementioned coupling agent, etc., and can be dissolved, and the specified substance can be obtained by filtrating in a clean room etc. as occasion demands.

[0025] As the production approach of the optical waveguide in this invention, a clad is [0026] as the example, although it differs a little in the case where the same ultraviolet-rays hardening resin as the case where usual macromolecule resin is used, and core material is used. (1) Apply resin with a refractive index smaller than the core used as a lower layer clad to the substrate of arbitration. Stoving etc. removes a solvent after spreading. When using ultraviolet-rays hardening resin here, it hardens by irradiating ultraviolet rays.

(2) Through the negative mask which applies the resin constituent of this invention used as a core on this, next has a waveguide pattern, irradiate ultraviolet rays and harden them. Then, this sample is developed with a dilute-alkali water solution, for example, 3% diethanolamine water solution, only the optical exposure section is hardened according to a mask pattern, and a waveguide pattern can be produced.

(3) After that, apply the macromolecule resin or ultraviolet-rays hardening resin for clads on this, and harden by solvent clearance or ultraviolet rays. It is more suitable it to be desirable that it is the same refractive index as for the clad of the core lateral portion formed in a lower layer clad and a list at the end here and the upper part, and to be the same ingredient. When ultraviolet-rays hardening resin is used for a clad, flattening of the maximum top-face front face can be carried out. In this case, what is necessary is to attain multilayer optical wiring, and just to repeat (2) and (3), when multilayering.

[Translation done.]

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

MEANS

[Means for Solving the Problem] The resin constituent for optical waveguides with which this invention person etc. uses a specific carboxyl group content epoxy compound (A) and epoxy group content compounds other than the (A) component (B) as a principal component as a result of wholeheartedly examination It can patternize [that a refractive index can be controlled somewhat freely by changing a presentation] by removing an unexposed part with a dilute-alkali water solution, It came to complete a header and this invention for excelling in light transmission nature, when it applies to the core section and the cladding layer of optical waveguide, and excelling in surface smoothness extremely.

[0005] Namely, this invention (1) In a molecule, at least two epoxy groups The carboxyl group content epoxy compound (A) which is a reactant of the epoxy compound (a) which it has, the compound (b) which has one carboxyl group and two hydroxyl groups in a molecule, and a polybasic acid anhydride (c), and epoxy group content compounds other than the (A) component And/or, it is related with the hardened material of the resin constituent for optical waveguides characterized by containing an oxetane compound (B) and an optical cationic initiator (C), and the resin constituent for optical waveguides given in (2) and (1).

[0006]

[The gestalt of operation of this invention] The resin constituents for optical waveguides of this invention are the carboxyl group content epoxy compound (A) which is a reactant of the epoxy compound (a) which has at least two epoxy groups in a molecule, the compound (b) which has one carboxyl group and two hydroxyl groups in a molecule, and a polybasic acid anhydride (c), epoxy group content compounds other than the (A) component and/or an oxetane compound (B), and mixture with an optical cationic initiator (C).

[0007] In this invention, a carboxyl group content epoxy compound (A) is used. A carboxyl group content epoxy compound (A) can be obtained by making the epoxy compound (a) which has at least two epoxy groups in a molecule, and the compound (b) which has one carboxyl group and two hydroxyl groups in a molecule react, and subsequently making a polybasic acid anhydride (c) react.

[0008] Here as an example of an epoxy compound (a) of having at least two epoxy groups in a molecule 3, 4-epoxycyclohexyl methyl -3, 4-epoxy cyclohexane carboxylate, 3, 4-epoxycyclohexyl ethyl -8, 4-epoxy cyclohexane carboxylate, 2-(3, 4-epoxycyclohexyl -5, 5-spiro -3, 4-epoxy) cyclohexane-m-dioxane, A bis(3, 4-epoxycyclohexyl) horse mackerel peat, a bis(3, 4-epoxycyclohexyl methyl) horse mackerel peat, As the bis(3, 4-epoxycyclohexyl) ether, a bis(3, 4-epoxycyclohexyl) diethyl siloxane, and a commercial item The Daicel Chemical Industries, Ltd. make, such as the SEROKI side 2021 (weight per epoxy equivalent 128-145) and the SEROKI side 2080 (weight per epoxy equivalent 190-210), 2 functionality alicyclic epoxy compound, EPOLEAD GT-301 (weight per epoxy equivalent 200-220), The Daicel Chemical Industries, Ltd. make, such as EPOLEAD GT-401 (weight per epoxy equivalent 210-235), 3 and 4 functionality alicyclic epoxy compound, EHPE (weight per epoxy equivalent 170-190, 70-90 degrees C of softening temperatures), Alicyclic epoxy compounds, such as the Daicel Chemical Industries, Ltd. make, such as EHPEL3150CE, and a solid alicyclic epoxy compound (a-1), The bisphenol A mold epoxy resin, a bisphenol female mold epoxy resin, Hydrogenation bisphenol A diglycidyl ether,

bisphenol hexafluoroacetone diglycidyl ether, Tetra-bromine bisphenol A diglycidyl ether, 1, 3-bis(1-(2, 3-epoxy propoxy)-1-trifluoromethyl - 2, 2, and 2-trifluoroethyl) benzene, 1, 4-bis(1-(2, 3-epoxy propoxy)-1-trifluoromethyl - 2, 2, and 2-trifluoroethyl) cyclohexyl, A 4 and 4'-bis(2, 3-epoxy propoxy) octafluoro biphenyl, Glycidyl ether compounds (a-2), such as a phenol novolak mold epoxy resin, a cresol novolak mold epoxy resin, and a tris phenol methane mold epoxy resin, etc. can be mentioned.

[0009] Moreover, as an example of a compound (b) of having one carboxyl group and two hydroxyl groups, dimethylol propionic acid, a dimethylol acetic acid, dimethylol butanoic acid, a dimethylol valeric acid, a dimethylol caproic acid, etc. can be mentioned into a molecule.

[0010] Furthermore, as an example of a polybasic acid anhydride (c), a maleic anhydride, a succinic anhydride, phthalic anhydride, tetrahydro phthalic anhydride, hexahydro phthalic anhydride, methyl hexahydro phthalic anhydride, trimellitic acid, etc. can be mentioned.

[0011] Making 0.05-0.7Eq of carboxyl groups in the above and a compound (b) react makes 0.1-0.5Eq react preferably desirable especially to 1Eq of epoxy groups in the above and an epoxy compound (a). (a) It is desirable to make 0.1-1.0Eq of anhydride radicals in a polybasic acid anhydride (c) react to 1Eq of hydroxyl groups in the reactant of a component and the (b) component.

[0012] It is desirable to use a catalyst, in order to promote a reaction, when making the above, the (a) component, and the (b) component react. As an example of the catalyst which can be used, they are benzyl dimethylamine, methyl triethyl ammoniumchloride, a triphenyl stibine, triphenyl phosphine, etc. As a desirable catalyst, triphenyl phosphine can be mentioned especially. (a) It is desirable by oxidizing with a peroxide etc. and making triphenyl phosphine after reaction termination of a component and the (b) component, and in reaction mixture into triphenyl phosphine oxide to inactivate the catalytic activity of triphenyl phosphine.

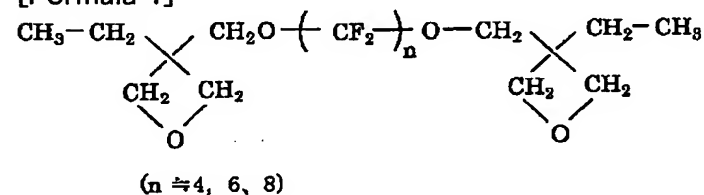
[0013] A diluent can also be used in a reaction. Solvents can be mentioned as an example of the diluent which can be used. As an example of solvents, ester, such as lactone, such as ether, such as aromatic hydrocarbon, such as ketones, such as ethyl methyl ketone and a cyclohexanone, toluene, and a xylene, and a tetrahydrofuran, gamma-butyrolactone, and epsilon-caprolactone, ethyl acetate, butyl acetate, carbitol acetate, and butyl-cellosolve acetate, can be mentioned. 70-110 degrees C is desirable especially desirable, and reaction temperature is 90-100 degrees C. 15 - 35 hours of reaction time are desirable.

[0014] (a) The reaction temperature of the hydroxyl group in the reactant of a component and the (b) component and the anhydride radical in the (c) component has desirable 70-110 degrees C, and 5 - 20 hours of reaction time are desirable.

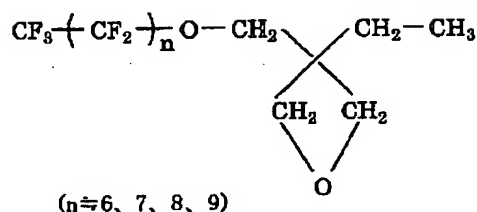
[0015] 10-100 are desirable especially desirable, and the acid numbers (mgKOH/g) of the carboxyl group content epoxy compound (A) which is an obtained product are 30-80. 200-700 are desirable especially desirable, and weight per epoxy equivalent is 250-500.

[0016] In this invention, the epoxy group content compounds and/or oxetane compounds (B) other than the (A) component are used. (B) As an example of a component, it is epoxy group content compound [, such as the above, an alicyclic epoxy compound (a-1), and a glycidyl ether compound (a-2),] (B-1), 3-ethyl-3-hydroxymethyloxetane, 1, and 4-bis[(3-ethyl-3-OKISETA nil methoxy) methyl] benzene and [0017].

[Formula 1]



[0018]



[0019] Oxetane compounds (B-2), such as a silicon denaturation oxetane compound, etc. can be mentioned.

[0020] An optical cationic initiator (C) is used in this invention. As an example of the optical cationic initiator (C) which can be used, if it reacts with an epoxy group by ultraviolet rays, although it is good, aromatic series iodonium salt, such as aromatic series sulfonium salt, such as aromatic series diazonium salt, such as P-methoxybenzene diazonium hexafluorophosphate, and triphenylsulfonium hexafluorophosphate, and diphenyliodonium hexafluorophosphate, aromatic series iodosyl salt, an aromatic series sulfoxonium salt, a metallocene compound, etc. will be mentioned anything, for example.

[0021] As an operating rate of the above and (A) - (C) component, among the resin constituent for optical waveguides of this invention (A) To the component 100 weight section, the 5 - 200 weight section is desirable especially desirable, and the (B) component is the 10 - 100 weight section, and receives the total amount 100 weight section of (A)+ (B) component. (C) 0.01 - 10 weight section is desirable especially desirable, and a component is 0.1 - 5 weight section.

[0022] In addition, in this invention, when required, optical cationic polymerization accelerators (an example, 9, a 10-dimethoxy-2-ethyl-anthracene, 9, 10-diethoxy anthracene, 2-ethyl thioxan ton, etc.), a silane coupling agent, a titanium system coupling agent, a flexible grant agent, a property modifier, etc. can be added. The property of a resin constituent can be reformed for these ingredients independent or by mixing and adding to a principal component.

[0023] for example, as an example of the silane coupling agent added in order to raise the adhesive property of the resin constituent of this invention gamma-aminopropyl trimethoxysilane, gamma-aminopropyl triethoxysilane, N-beta-(aminoethyl)-gamma-aminopropyl trimethoxysilane, N-beta-(aminoethyl)-gamma-aminopropyl triethoxysilane, N-beta-(aminoethyl)-beta-(aminoethyl)-gamma-aminopropyl methyl dimethoxysilane, gamma-mercapto propyltrimethoxysilane, gamma-mercapto propyl triethoxysilane, Gamma-methacryloxypropyl trimethoxy silane, gamma-glycidoxypropyltrimethoxysilane, A N-beta-(N-vinylbenzyl aminoethyl)-gamma-aminopropyl trimethoxysilane hydrochloride, Methyl trimethoxysilane, methyl triethoxysilane, vinyltriacetoxysilane, Gamma-chloropropyltrimethoxysilane, hexamethyldisilazane, gamma-ANIRINO propyltrimethoxysilane, vinyltrimethoxysilane, Octadecyl dimethyl [3-(trimethoxysilyl) propyl] ammoniumchloride, gamma-chloropropyl methyl dimethoxysilane, gamma-mercaptpropylmethyl dimethoxysilane, Methyltrichlorosilane, vinyltriethoxysilane, gamma-methacryloxypropyl tris (2-methoxyethoxy) silane, beta-(3, 4-epoxycyclohexyl) ethyltrimethoxysilane, etc. are mentioned.

[0024] The resin constituent of this invention can mix (A) - (C) component, the aforementioned coupling agent, etc., and can be dissolved, and the specified substance can be obtained by filtrating in a clean room etc. as occasion demands.

[0025] As the production approach of the optical waveguide in this invention, a clad is [0026] as the example, although it differs a little in the case where the same ultraviolet-rays hardening resin as the case where usual macromolecule resin is used, and core material is used. (1) Apply resin with a refractive index smaller than the core used as a lower layer clad to the substrate of arbitration. Stoving etc. removes a solvent after spreading. When using ultraviolet-rays hardening resin here, it hardens by irradiating ultraviolet rays.

(2) Through the negative mask which applies the resin constituent of this invention used as a core on this, next has a waveguide pattern, irradiate ultraviolet rays and harden them. Then, this sample is developed with a dilute-alkali water solution, for example, 3% diethanolamine water solution, only the optical exposure section is hardened according to a mask pattern, and a waveguide pattern can be produced.

(3) After that, apply the macromolecule resin or ultraviolet-rays hardening resin for clads on this, and harden by solvent clearance or ultraviolet rays. It is more suitable. it to be desirable that it is the same refractive index as for the clad of the core lateral portion formed in a lower layer clad and a list at the end here and the upper part, and to be the same ingredient. When ultraviolet-rays hardening resin is used for a clad, flattening of the maximum top-face front face can be carried out. In this case, what is necessary is to attain multilayer optical wiring, and just to repeat (2) and (3), when multilayering.

[Translation done.]

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.**** shows the word which can not be translated.

3.In the drawings, any words are not translated.

EXAMPLE

[Example] Hereafter, although an example explains this invention still more concretely, this invention is not limited to these examples.

Hydrogenation bisphenol A diglycidyl ether 353g, (Synthetic example 1 of a carboxyl group content epoxy compound (A)) 80.4g [of dimethylol propionic acid] and triphenyl phosphine 0.8g is taught. A reaction will be ended, if it reacts at 95 degrees C for about 10 hours and the acid number (mgKOH/g) of reaction mixture becomes 0.5 or less. Subsequently, tert-butyl peroxide 2-ethylhexyl carbonate 0.8g is taught at 80 degrees C. It reacted for about 3 hours, and triphenyl phosphine in reaction mixture was oxidized to triphenyl phosphine oxide, subsequently 60g of succinic anhydrides was taught at 90 degrees C, it reacted for about 5 hours, and the product (A-1) of weight per epoxy equivalent 353 and the acid number (mgKOH/g) 68.3 was obtained.

[0028] The resin constituent (a) prepared from product [which were obtained in the example 1 of example 1 composition] (A-1)g [70] and 3, 4-epoxycyclohexyl methyl -3, and 4-epoxy cyclohexane carboxylate 20g, bisphenol A diglycidyl ether 10g, and screw [4-(diphenyl sulfonium) phenyl] sulfide-screw hexafluorophosphate 3g was prepared. The refractive index after hardening of this resin constituent (a) was 1.519 on the wavelength of 589nm.

[0029] 60g (A-1) of next, products obtained in the synthetic example 1 on the silicon substrate, EPOLEAD GT-301(Daicel Chemical Industries, Ltd. make, weight-per-epoxy-equivalent 210, 3 functionality alicyclic epoxy compound) 5g, 1, 3-screw (1-(2, 3-epoxy propoxy)-1-trifluoromethyl - 2, 2, and 2-trifluoroethyl) The resin constituent (b) prepared from benzene 35g and screw [4-(diphenyl sulfonium) phenyl] sulfide-screw hexafluorophosphate 3g It applied with the spin coat, ultraviolet rays were irradiated two times 2500 mJ/cm all over the, and the 10-micrometer lower cladding layer was produced.

[0030] Next, the above and a resin constituent (a) were applied to the thickness of 5 micrometers with the spin coat on this lower cladding layer. In addition, the refractive index after hardening of a lower cladding layer was 1.491 on the wavelength of 589nm.

[0031] Next, ultraviolet rays were irradiated through the negative mask which has a waveguide pattern, this sample was developed in the diethanolamine water solution 3% after that, and the waveguide pattern was produced. Then, on this waveguide pattern and a lower cladding layer, the above and a resin constituent (b) were applied to the thickness of 15 micrometers, ultraviolet rays are irradiated, and were stiffened, and optical waveguide was produced. The multimode channel waveguide which has the core which consists of a hardened material of the resin constituent (a) of the lower cladding layer, up cladding layer, and refractive index 1.530 which consist of a hardened material of the resin constituent (b) of the refractive index 1.515 after hardening by this actuation was producible. It was 0.30 dB/cm, as a result of starting the obtained optical waveguide in die length of 5cm and investigating photoconductive wave loss using helium-Ne laser light with a wavelength of 633nm.

[Translation done.]

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開2003-147045

(P2003-147045A)

(43) 公開日 平成15年5月21日 (2003.5.21)

(51) Int.Cl.⁷

識別記号

F I

テームト* (参考)

C 0 8 G 59/16

C 0 8 G 59/16

2 H 0 4 7

G 0 2 B 6/12

G 0 2 B 6/12

N 4 J 0 3 6

審査請求 未請求 請求項の数 2 O L (全 5 頁)

(21) 出願番号 特願2001-350739 (P2001-350739)

(22) 出願日 平成13年11月15日 (2001.11.15)

(71) 出願人 000004086

日本化薬株式会社

東京都千代田区富士見1丁目11番2号

(72) 発明者 小柳 敬夫

東京都板橋区赤塚3-31-9

(72) 発明者 横島 実

茨城県取手市井野台4-6-32

Fターム (参考) 2H047 PA02 PA15 PA24 PA28 QA05

4J036 AC02 AD05 AD08 AF06 AJ08

CA22 CA25 CA28 CB03 CB07

CC02 GA03 GA22 GA25 GA29

HA02 JA07 JA15

(54) 【発明の名称】 光導波路用樹脂組成物及びその硬化物

(57) 【要約】

【課題】 導波路形成工程が容易で、多層の光配線が可能な光導波路用樹脂組成物及びその硬化物を提供する。

【解決手段】 特定のカルボキシル基含有エポキシ化合物 (A) と (A) 成分以外のエポキシ基含有化合物及び／又はオキセタン化合物 (B) と光カチオン重合開始剤 (C) を含有することを特徴とする光導波路用樹脂組成物。

【特許請求の範囲】

【請求項1】分子中に少なくとも2個のエポキシ基を有するエポキシ化合物(a)と分子中に1個のカルボキシル基と2個の水酸基を有する化合物(b)と多塩基酸無水物(c)の反応物であるカルボキシル基含有エポキシ化合物(A)と(A)成分以外のエポキシ基含有化合物及び/又はオキセタン化合物(B)と光カチオン重合開始剤(C)を含有することを特徴とする光導波路用樹脂組成物

【請求項2】請求項1記載の光導波路用樹脂組成物の硬化物

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、一般光学や微小光学分野で、さらに光通信や光情報処理の分野で用いられる種々の光集積回路または光配線板等に利用できる光導波路用樹脂組成物及びその硬化物に関する。

【0002】

【従来の技術】光情報処理、光通信分野で用いる光導波路は、集積化、微小化、高機能化、低価格化をめざして、近年、検討が盛んになってきている。実際に、石英系光導波路が光通信分野の一部では実用化されるに至っている。また、安価な材料を用いて、簡便な作製法が選択できる高分子導波路の検討も盛んである。例えば、リソグラフィやエッチングなど半導体加工に用いる方法の適用や感光性高分子あるいはレジストを用いる方法を挙げることができる。特に感光性高分子を用いてコアを形成して導波路を形成する方法においては、パターンフィルムを通して紫外線を照射し、未露光部を溶剤類で除去して形成する方法等が行なわれ、その作製方法が簡便で低価格化には適しているが、パターン化するのに溶剤を使用する必要があり安全及び環境の問題があり、又感光性高分子の透明性が不十分で吸収損失が高かったり、作製されるコア形状の均一性、再現性に問題があって、散乱損失が高くなることがあり、その導波路特性が石英系光導波路と同程度の性能を有する光導波路は作製されていない。

【0003】

【発明が解決しようとする課題】本発明の目的は、上述した課題を解決し、希アルカリ水溶液でパターン化することが可能で、加工性に優れる低価格と高性能化を同時に満足する光導波路用樹脂組成物及びその硬化物を提供することにある。

【0004】

【課題を解決するための手段】本発明者等は、鋭意検討の結果、特定のカルボキシル基含有エポキシ化合物

(A)と(A)成分以外のエポキシ基含有化合物(B)を主成分とする光導波路用樹脂組成物は、組成を変えることにより屈折率をある程度自由に制御できること、未露光部を希アルカリ水溶液により除去することによりパ

ターン化できること、光導波路のコア部やクラッド層に適用したとき光透過性に優れ、且つ平坦性に極めて優れていることを見出し、本発明を完成するに至った。

【0005】すなわち、本発明は、(1)分子中に少なくとも2個のエポキシ基を有するエポキシ化合物(a)と分子中に1個のカルボキシル基と2個の水酸基を有する化合物(b)と多塩基酸無水物(c)の反応物であるカルボキシル基含有エポキシ化合物(A)と(A)成分以外のエポキシ基含有化合物及び/又はオキセタン化合物(B)と光カチオン重合開始剤(C)を含有することを特徴とする光導波路用樹脂組成物、(2)(1)記載の光導波路用樹脂組成物の硬化物、に関する。

【0006】

【本発明の実施の形態】本発明の光導波路用樹脂組成物は、分子中に少なくとも2個のエポキシ基を有するエポキシ化合物(a)と分子中に1個のカルボキシル基と2個の水酸基を有する化合物(b)と多塩基酸無水物

(c)の反応物であるカルボキシル基含有エポキシ化合物(A)と(A)成分以外のエポキシ基含有化合物及び/又はオキセタン化合物(B)及び光カチオン重合開始剤(C)との混合物である。

【0007】本発明では、カルボキシル基含有エポキシ化合物(A)を使用する。カルボキシル基含有エポキシ化合物(A)は、分子中に少なくとも2個のエポキシ基を有するエポキシ化合物(a)と分子中に1個のカルボキシル基と2個の水酸基を有する化合物(b)を反応させ、次いで多塩基酸無水物(c)を反応させることにより得ることができる。

【0008】ここで、分子中に少なくとも2個のエポキシ基を有するエポキシ化合物(a)の具体例としては、3,4-エポキシシクロヘキシルメチル-3,4-エポキシシクロヘキサンカルボキシレート、3,4-エポキシシクロヘキシルエチル-8,4-エポキシシクロヘキサンカルボキシレート、2-(3,4-エポキシシクロヘキシル-5,5-スピロ-3,4-エポキシ)シクロヘキサン-m-ジオキサン、ビス(3,4-エポキシシクロヘキシル)アジペート、ビス(3,4-エポキシシクロヘキシルメチル)アジペート、ビス(3,4-エポキシシクロヘキシル)エーテル、ビス(3,4-エポキシシクロヘキシル)ジエチルシロキサン、市販品としては、セロキサイド2021(エポキシ当量128~145)、セロキサイド2080(エポキシ当量190~210)などのダイセル化学工業(株)製、2官能性脂環式エポキシ化合物、エポリッドGT-301(エポキシ当量200~220)、エポリッドGT-401(エポキシ当量210~235)などのダイセル化学工業

(株)製、3及び4官能性脂環式エポキシ化合物、EHPE(エポキシ当量170~190、軟化点70~90℃)、EHPEL3150CEなどのダイセル化学工業(株)製、固形の脂環式エポキシ化合物等の脂環式エポ

キシ化合物(a-1)、ビスフェノールA型エポキシ樹脂、ビスフェノールF型エポキシ樹脂、水添ビスフェノールAジグリシジルエーテル、ビスフェノールヘキサフルオロアセトンジグリシジルエーテル、テトラブromビスフェノールAジグリシジルエーテル、1,3-ビス(1-(2,3-エポキシプロポキシ)-1-トリフルオロメチル-2,2,2-トリフルオロエチル)ベンゼン、1,4-ビス(1-(2,3-エポキシプロポキシ)-1-トリフルオロメチル-2,2,2-トリフルオロエチル)シクロヘキシル、4,4'-ビス(2,3-エポキシプロポキシ)オクタフルオロビフェニル、フェノール・ノボラック型エポキシ樹脂、クレゾール・ノボラック型エポキシ樹脂、トリスフェノールメタン型エポキシ樹脂等のグリシジルエーテル化合物(a-2)等を挙げることができる。

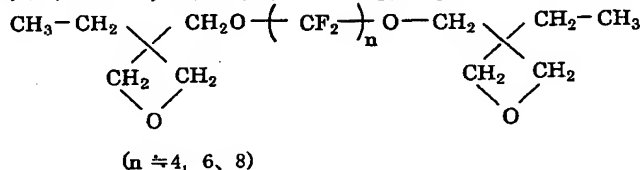
【0009】また、分子中に1個のカルボキシル基と2個の水酸基を有する化合物(b)の具体例としては、ジメチロールプロピオン酸、ジメチロール酢酸、ジメチロール酪酸、ジメチロール吉草酸、ジメチロールカブロン酸等を挙げることができる。

【0010】更に、多塩基酸無水物(c)の具体例としては、無水マレイン酸、無水コハク酸、無水フタル酸、テトラヒドロ無水フタル酸、ヘキサヒドロ無水フタル酸、メチルヘキサヒドロ無水フタル酸、トリメリット酸等を挙げることができる。

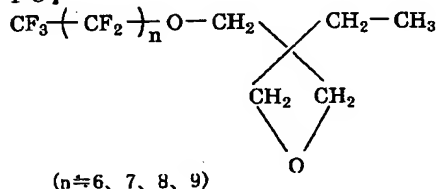
【0011】前記、エポキシ化合物(a)中のエポキシ基1当量に対して、前記、化合物(b)中のカルボキシル基0.05~0.7当量を反応させるのが好ましく、特に好ましくは0.1~0.5当量を反応させる。

(a)成分と(b)成分の反応物中の水酸基1当量に対して、多塩基酸無水物(c)中の無水物基0.1~1.0当量を反応させるのが好ましい。

【0012】前記、(a)成分と(b)成分を反応させる場合、反応を促進するために、触媒を使用するのが好ましい。使用しうる触媒の具体例としては、ベンジルジメチルアミン、メチルトリエチルアンモニウムクロライ



【0018】



【0019】、シリコン変性オキセタン化合物等のオキ

ド、トリフェニルスチビン、トリフェニルホスフィン等である。特に好ましい触媒としては、トリフェニルホスフィンを挙げることができる。(a)成分と(b)成分の反応終了後、反応液中のトリフェニルホスフィンを過酸化物等により酸化し、トリフェニルホスフィンオキサイドにすることによりトリフェニルホスフィンの触媒活性を不活性化することが好ましい。

【0013】反応に当たり、希釈剤を使用することもできる。使用しうる希釈剤の具体例としては、溶剤類を挙げることができる。溶剤類の具体例としては、エチルメチルケトン、シクロヘキサノン等のケトン類、トルエン、キシレン等の芳香族炭化水素、テトラヒドロフラン等のエーテル類、γ-ブチロラクトン、ε-カプロラクトン等のラクトン類、酢酸エチル、酢酸ブチル、カルビトールアセテート、ブチルセロソルブアセテート等のエステル類等を挙げることができる。反応温度は70~110℃が好ましく、特に好ましくは90~100℃である。反応時間は、15~35時間が好ましい。

【0014】(a)成分と(b)成分の反応物中の水酸基と(c)成分中の無水物基の反応温度は70~110℃が好ましく、反応時間は、5~20時間が好ましい。

【0015】得られた生成物であるカルボキシル基含有エポキシ化合物(A)の酸価(mg KOH/g)は、10~100が好ましく、特に好ましくは30~80である。エポキシ当量は200~700が好ましく、特に好ましくは250~500である。

【0016】本発明では、(A)成分以外のエポキシ基含有化合物及び/又はオキセタン化合物(B)を使用する。(B)成分の具体例としては、前記、脂環式エポキシ化合物(a-1)やグリシジルエーテル化合物(a-2)等のエポキシ基含有化合物(B-1)、3-エチル-3-ヒドロキシメチルオキセタン、1,4-ビス[(3-エチル-3-オキセタニルメトキシ)メチル]ベンゼン、

【0017】

【化1】

セタン化合物(B-2)等を挙げることができる。

【0020】本発明では、光カチオン重合開始剤(C)を使用する。使用しうる光カチオン重合開始剤(C)の具体例としては、紫外線によりエポキシ基と反応するものであれば何でもよいが、例えば、P-メトキシベンゼンジアゾニウムヘキサフルオロホスフェート等の芳香族ジアゾニウム塩、トリフェニルスルホニウムヘキサフルオロホスフェート等の芳香族スルホニウム塩、ジフェニ

ルヨードニウムヘキサフルオロホスフェート等の芳香族ヨードニウム塩、芳香族ヨードシル塩、芳香族スルホキソニウム塩、メタロセン化合物などが挙げられる。

【0021】本発明の光導波路用樹脂組成物中、前記、(A)～(C)成分の使用割合としては、(A)成分100重量部に対して、(B)成分は5～200重量部が好ましく、特に好ましくは10～100重量部であり、(A)＋(B)成分の総量100重量部に対して、(C)成分は、0.01～10重量部が好ましく、特に好ましくは、0.1～5重量部である。

【0022】なお、本発明において、必要な場合は、光カチオン重合促進剤(例、9,10-ジメトキシ-2-エチルアントラセン、9,10-ジエトキシアントラセン、2-エチルチオキサントン等)、シランカップリング剤、チタン系カップリング剤、可とう性付与剤、特性改質剤等を加えることができる。これらの材料を単独あるいは混合して主成分に加えることにより樹脂組成物の特性を改質することができる。

【0023】例えば、本発明の樹脂組成物の接着性を高めるために加えるシランカップリング剤の具体例としては、 γ -アミノプロピルトリメトキシシラン、 γ -アミノプロピルトリエトキシシラン、N- β -(アミノエチル)- γ -アミノプロピルトリメトキシシラン、N- β -(アミノエチル)- γ -アミノプロピルトリエトキシシラン、N- β -(アミノエチル)- β -(アミノエチル)- γ -アミノプロピルメチルジメトキシシラン、 γ -メルカプトプロピルトリメトキシシラン、 γ -メルカプトプロピルトリエトキシシラン、 γ -メタクリロキシプロピルトリメトキシシラン、 γ -グリシドキシプロピルトリメトキシシラン、N- β -(N-ビニルベンジルアミノエチル)- γ -アミノプロピルトリメトキシシラン塩酸塩、メチルトリメトキシシラン、メチルトリエトキシシラン、ビニルトリアセトキシシラン、 γ -クロロプロピルトリメトキシシラン、ヘキサメチルジシラザン、 γ -アニリノプロピルトリメトキシシラン、ビニルトリメトキシシラン、オクタデシルジメチル[3-(トリメトキシシリル)プロピル]アンモニウムクロライド、 γ -クロロプロピルメチルジメトキシシラン、 γ -メルカプトプロピルメチルジメトキシシラン、メチルトリクロロシラン、ビニルトリエトキシシラン、 γ -メタクリロキシプロピルトリス(2-メトキシエトキシ)シラン、 β -(3,4-エポキシシクロヘキシル)エチルトリメトキシシランなどが挙げられる。

【0024】本発明の樹脂組成物は、(A)～(C)成分及び前記のカップリング剤等を混合、溶解し、必要により、クリーンルーム内等で口過をすることにより、目的物を得ることができる。

【0025】本発明における光導波路の作製方法としてはクラッドは通常の高分子樹脂を用いる場合とコア材と同様の紫外線硬化樹脂を用いる場合では若干異なるがそ

の一例として、

【0026】(1)任意の基板に下層クラッドとなるコアよりも屈折率の小さな樹脂を塗布する。塗布後、加熱乾燥などにより溶媒を除去する。ここに紫外線硬化樹脂を用いるときは紫外線を照射することにより硬化する。

(2)この上にコアとなる本発明の樹脂組成物を塗布し、次に、導波路パターンを有するネガマスクを介して紫外線を照射し硬化する。その後、この試料を希アルカリ水溶液、例えば3%ジエタノールアミン水溶液で現像し、マスクパターンに従い、光照射部のみ硬化し、導波路パターンが作製できる。

(3)その後、この上にクラッド用的高分子樹脂又は紫外線硬化樹脂を塗布し、溶媒除去又は紫外線により硬化する。ここで下層クラッド、並びに最後に形成するコア側面部及び上部のクラッドは同じ屈折率であることが望ましく、同一の材料である方が好適である。クラッドに紫外線硬化樹脂を用いた場合、最上面表面を平坦化できる。この場合、多層の光配線が可能になり、多層化を行う場合は(2)、(3)を繰り返せばよい。

【0027】

【実施例】以下、本発明を実施例によりさらに具体的に説明するが、本発明は、これらの実施例に限定されない。

(カルボキシル基含有エポキシ化合物(A)の合成例1)水添ビスフェノールAジグリシジルエーテル353g、ジメチロールプロピオン酸80.4g及びトリフェニルホスフィン0.8gを仕込み、95℃で約10時間反応し、反応液の酸価(mg KOH/g)が0.5以下になったら反応を終了し、次いで80℃でt-ブチルパーオキシ2-エチルヘキシルカーボネート0.8gを仕込み、約3時間反応し、反応液中のトリフェニルホスフィンをトリフェニルホスフィンオキサイドに酸化し、次いで90℃で無水コハク酸60gを仕込み、約5時間反応し、エポキシ当量353、酸価(mg KOH/g)68.3の生成物(A-1)を得た。

【0028】実施例1

合成例1で得た生成物(A-1)70g、3,4-エポキシシクロヘキシルメチル-3,4-エポキシシクロヘキサンカルボキシレート20g、ビスフェノールAジグリシジルエーテル10g及びビス[4-(ジフェニルホルモニウム)フェニル]スルフィド-ビスヘキサフルオロホスフェート3gから調製した樹脂組成物(a)を準備した。この樹脂組成物(a)の硬化後の屈折率は波長589nmで1.519であった。

【0029】次に、シリコン基板上に、合成例1で得た生成物(A-1)60g、エポリドGT-301(ダイセル化学工業(株)製、エポキシ当量210、3官能性脂環式エポキシ化合物)5g、1,3-ビス(1-(2,3-エポキシプロポキシ)-1-トリフルオロメチル-2,2,2-トリフルオロエチル)ベンゼン35

g 及びビス〔4- (ジフェニルスルホニウム) フェニル〕スルフィド-ビスヘキサフルオロホスフェート 3 g から調製した樹脂組成物 (b) をスピンコートにより塗布して、その全面に紫外線を 2500 mJ/cm^2 照射して $10 \mu\text{m}$ の下部クラッド層を作製した。

【0030】次に、この下部クラッド層の上に、前記、樹脂組成物 (a) をスピンコートにより $5 \mu\text{m}$ の厚さに塗布した。なお、下部クラッド層の硬化後の屈折率は波長 589 nm で 1.491 であった。

【0031】次に、導波路パターンを有するネガマスクを介して紫外線を照射し、その後、この試料を 3% ジエタノールアミン水溶液で現像し、導波路パターンを作製した。その後、この導波路パターンおよび下部クラッド層の上に、前記、樹脂組成物 (b) を $15 \mu\text{m}$ の厚さに

塗布し、紫外線を照射して硬化させ、光導波路を作製した。この操作により硬化後の屈折率 1.515 の樹脂組成物 (b) の硬化物からなる下部クラッド層と上部クラッド層および屈折率 1.530 の樹脂組成物 (a) の硬化物からなるコアを有するマルチモードチャンネル導波路が作製できた。得られた光導波路を 5 cm の長さに切り出し、波長 633 nm の He-Ne レーザー光を用いて光導波損失を調べた結果、 0.30 dB/cm であった。

【0032】

【発明の効果】本発明にかかる光導波路の作製は簡易で、高品質な高分子光導波路の得られる樹脂組成物である。したがって、本発明の光導波路用樹脂組成物は、量産が必要とする光導波路型部品への適用が有利である。